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(54) **Polyethylene stabilizer compositions comprising compounds with piperidine groups and metal compounds**

**Polyäthylen-Stabilisatorzusammensetzungen aus Verbindungen mit Piperidingruppen und Metallverbindungen**

**Compositions stabilisantes de polyéthylène à base de composés avec des groupements de pipéridine et composés de métal**

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(56) References cited:  
**GB-A- 2 132 621**

• **PATENT ABSTRACTS OF JAPAN, vol. 11, no. 124 (C-416)[2571], 17th April 1987; & JP-A-61 261 332 (SUMITOMO NAUGATUCK CO., LTD) 19-11-1986**

**EP 0 290 388 B1**

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## Description

The present invention relates to a novel method for stabilizing polyethylene against photooxidative degradation by using mixtures of 2,2,6,6-tetramethylpiperidine derivatives and particular metal compounds.

Polyethylene is here to be understood as meaning linear or branched polymers of ethylene of low, medium and high density, their mixtures in any proportions and also ethylene copolymers with aliphatic  $C_3$ - $C_{12}$ - $\alpha$ -olefines containing up to 20% of di- $\alpha$ -olefine.

Of particular interest are branched low-density polyethylene, generally known as LDPE, and linear low-density polyethylene, generally designated as LLDPE, and their mixtures in any proportion.

It is known that polyethylene undergoes a progressive decrease in mechanical strength up to embrittlement when it is exposed to sunlight, as a result of photooxidative degradation caused by ultraviolet radiation.

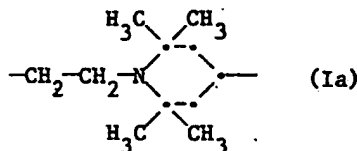
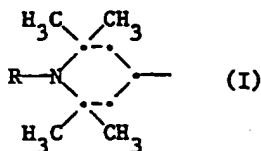
To overcome this drawback it is necessary to add to the polymer suitable light stabilizers, for example certain derivatives of benzophenone and benzotriazole, nickel complexes, esters of substituted benzoic acids or sterically hindered amines.

Certain 2,2,6,6-tetramethylpiperidine derivatives of relatively high molecular weight have recently shown remarkable efficacy; nevertheless, the results obtained with these compounds have not been completely satisfactory, so that a further improvement was desirable.

It has now been found surprisingly that, when particular mixtures of one or more 2,2,6,6-tetramethylpiperidine derivatives with one or more metal compounds are used, light stability values are obtained which are significantly higher than those given by the use of piperidine compounds alone.

In particular, the present invention relates to a novel method for stabilizing polyethylene, which comprises the use of synergistic mixtures composed of

(A) one or more compounds with groups of the formula (I) or (Ia)



in which R is hydrogen,  $C_1$ - $C_4$ -alkyl, allyl, benzyl, acetyl, acryloyl, 2-hydroxyethyl or 2-hydroxypropyl, said piperidine group of formula (I) not being bound in the 4-position to an oxygen atom, preferably hydrogen or methyl, and (B) one or more metal compounds selected from oxides and hydroxides of Al, Mg and Zn, preferably Mg and Zn.

If appropriate, the following can be added to the mixtures of (A)+(B):

(C) one or more salts of Al, Ba, Ca, Mg, Sr and Zn with  $C_1$ - $C_{22}$ -carboxylic acids, preferably the salts of Al, Ca, Mg or Zn with  $C_{12}$ - $C_{18}$ -carboxylic acids. The use of certain 2,2,6,6-tetramethylpiperidine derivatives mixed with oxides or hydroxides of Mg or Zn as stabilizers for polymers was already known, but was restricted to the stabilization of polyurethanes.

In particular, Japanese Patent 82-34,155, published on 24.2.1982, claims the stabilization of polyurethanes with mixtures comprising esters of 2,2,6,6-tetramethyl-4-piperidinol, oxides or hydroxides of Mg or Zn and organic phosphites. The said mixtures do not give satisfactory results when used for stabilizing polyethylene.

D.S. Carr and B. Baum (Modern Plastics, 7/1981, p. 64-68; C.A. 95, 81924) describe a light stabilizing system based on the combination of zinc dimethyl- or diethyl-dithiocarbamate and zinc oxide for use in plastics.

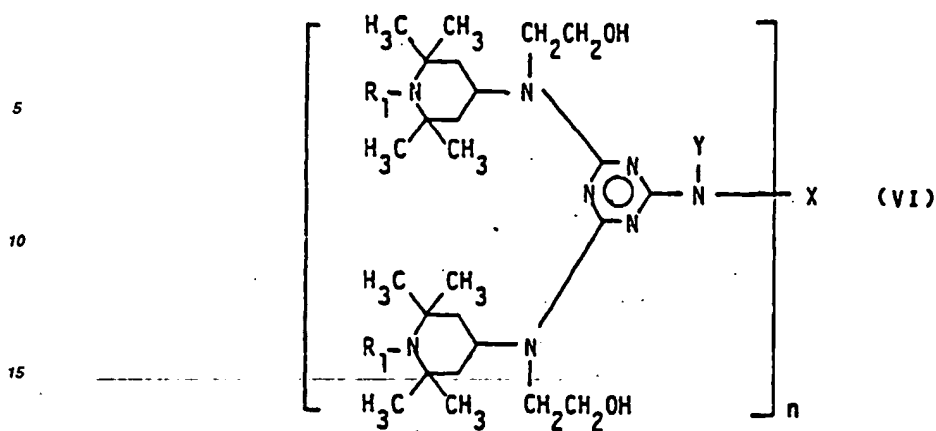
On the other hand, British Patent 2,132,621 describes the use of mixtures of zinc oxide and esters of 2,2,6,6-tetramethyl-4-piperidinol as photodegrading agents for polyolefines, in particular polyethylene and polypropylene.

The synergistic light stabilizing effect, obtained with the mixtures of the present invention, on polyethylene is therefore surprising.

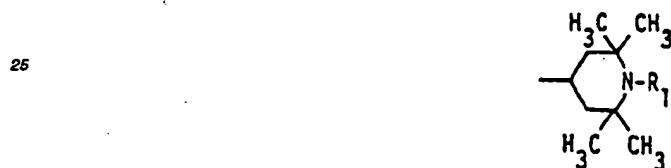
Compounds (A) which contain the group of the formula (I) or (Ia) and can be used according to the present invention are:

(A1) The compounds claimed in US Patent 4,086,204, preferably those of the formula (II)





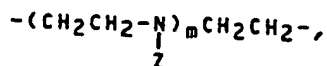
20 in which  $R_1$  is hydrogen or methyl,  $n$  is 1 or 2, with  $n = 1$   $X$  is  $C_1$ - $C_{12}$ -alkyl, benzyl or  $-CH_2CH_2OH$  and  $Y$  is hydrogen or a group



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and with  $n = 2$   $X$  is  $C_2$ - $C_6$ -alkylene, xylylene or a group

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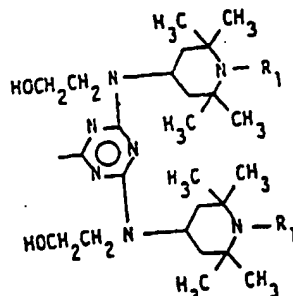


where  $m$  is 1 or 2 and  $Z$  is a group of the formula

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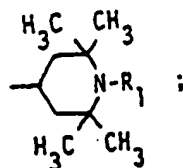
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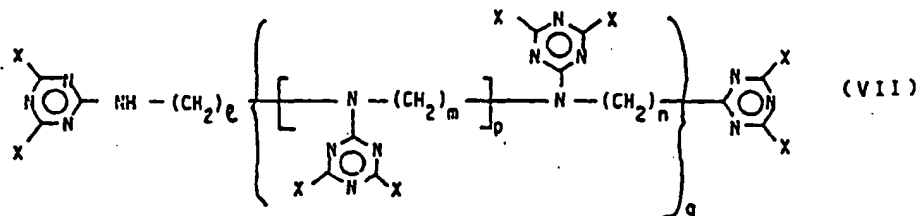


and  $Y$  is hydrogen or a group

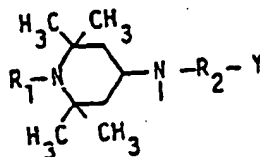
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(A6) The compounds claimed in European Patent 29,522, preferably those of the formula (VII)

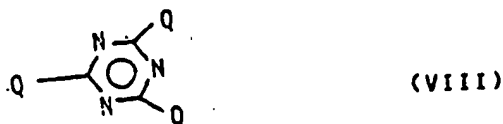


in which l, m, n are 2 or 3, p and q are zero or 1 and X is a group

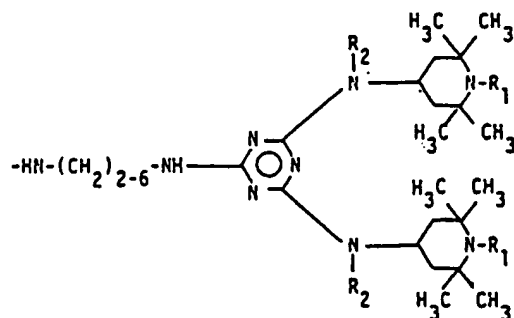


where R<sub>1</sub> is hydrogen or methyl, R<sub>2</sub> is C<sub>2</sub>-C<sub>3</sub>-alkylene and Y is OH, C<sub>1</sub>-C<sub>8</sub>-alkoxy, dimethylamino or diethylamino;

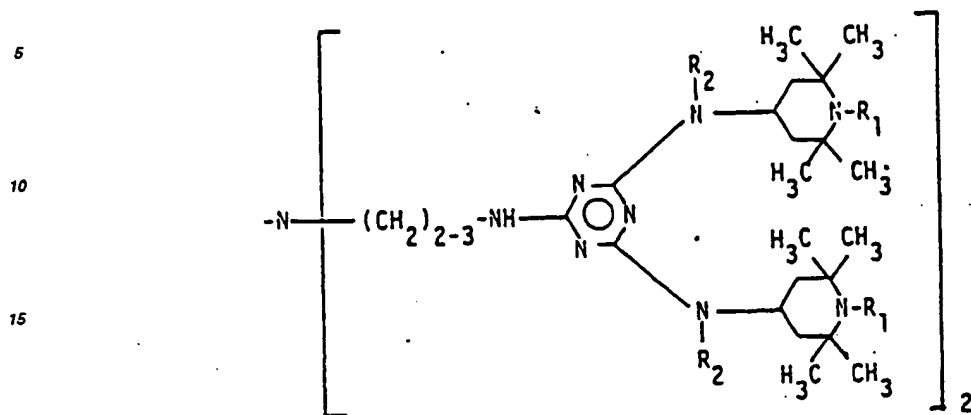
(A7) The compounds claimed in US Patent 4,288,593, preferably those of the formula (VIII)



in which Q is a group of the formula

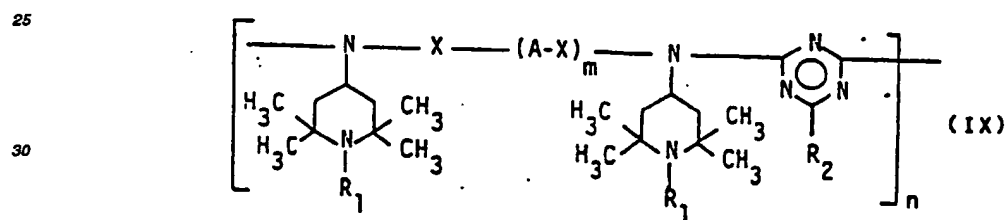


or a group of the formula



where  $R_1$  is hydrogen or methyl and  $R_2$  is  $C_1$ - $C_8$ -alkyl;

(AB) The compounds claimed in US Patent 4,315,859, preferably those of the formula (IX)



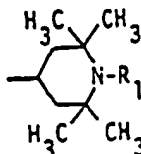
in which  $R_1$  is hydrogen or methyl, X is  $C_2$ - $C_6$ -alkylene, A is -O-, -NH- or



m is 1 or 2,  $R_2$  is morpholino, hexamethyleneimino, -OR<sub>3</sub> or

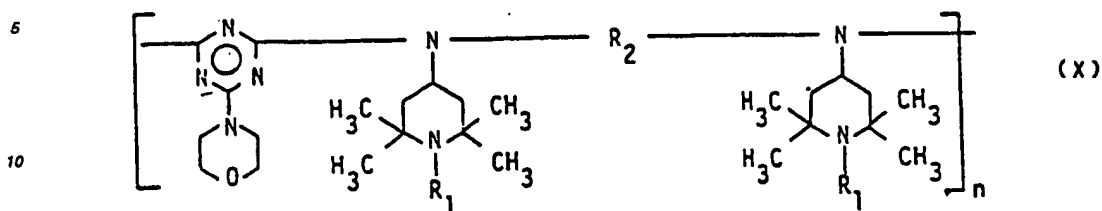


where  $R_3$  is  $C_1$ - $C_8$ -alkyl allyl, cyclohexyl, phenyl or benzyl and  $R_4$  and  $R_5$  which can be identical or different are  $C_1$ - $C_8$ -alkyl which may be interrupted by an oxygen atom, allyl, cyclohexyl, 2-hydroxyethyl, benzyl or a group



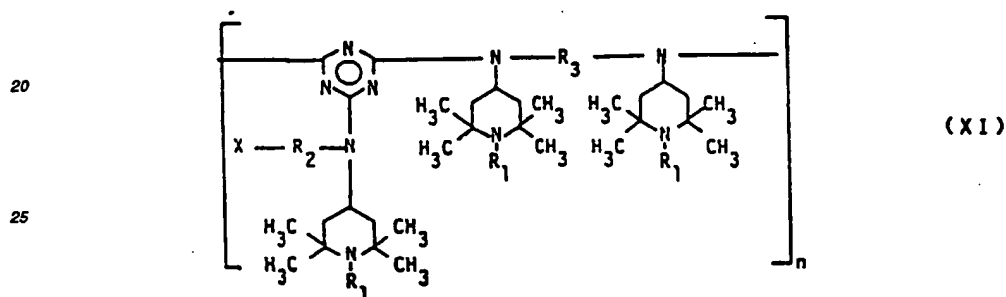
and  $R_5$  can also be hydrogen;

(A9) The compounds claimed in US Patent 4,331,586, preferably those of the formula (X)



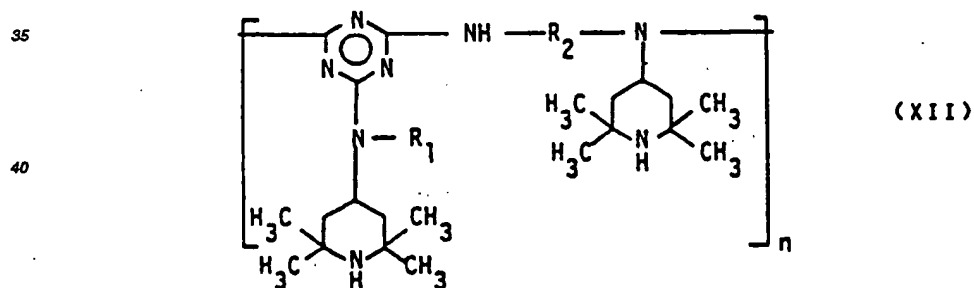
in which  $R_1$  is hydrogen or methyl,  $R_2$  is  $C_2$ - $C_6$ -alkylene and  $n$  is a number from 2 to 20;

15 (A10) The compounds claimed in European Patent 24,338, preferably those of the formula (XI)



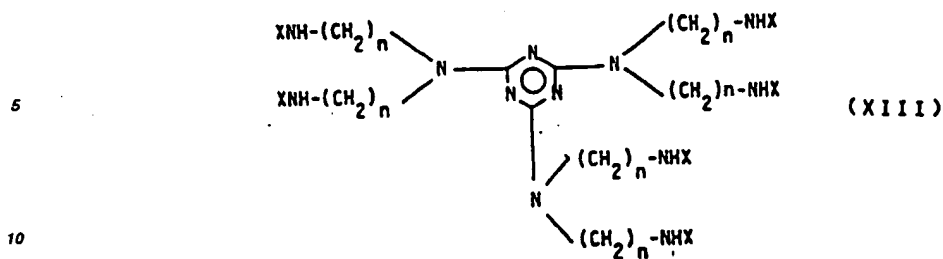
30 in which  $R_1$  is hydrogen or methyl,  $R_2$  is  $C_2$ - $C_3$ -alkylene,  $X$  is  $C_1$ - $C_6$ -alkoxy, dimethylamino or diethylamino,  $R_3$  is  $C_2$ - $C_6$ -alkylene and  $n$  is a number from 2 to 20;

(A11) The compounds claimed in European Patent 42,554, preferably those of the formula (XII)

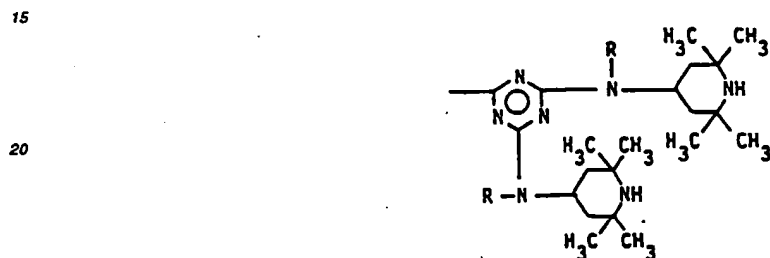


in which  $R_1$  is  $C_1$ - $C_8$ -alkyl,  $C_6$ - $C_8$ -cycloalkyl,  $(C_1-C_4)$ -alkoxy propyl, dimethylaminopropyl or diethylaminopropyl,  $R_2$  is  $C_2$ - $C_6$ -alkylene and  $n$  is a number from 2 to 20;

50 (A12) The compounds claimed in European Patent 44,499, preferably those of the formula (XIII)

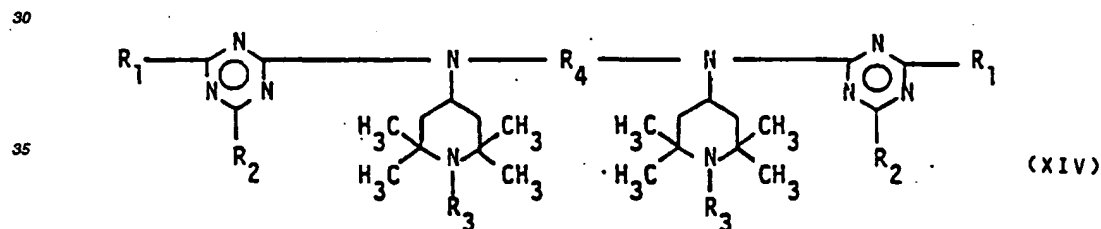


in which n is 2 or 3 and X is a group of the formula



where R is hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>2</sub>-C<sub>4</sub>-alkyl substituted by C<sub>1</sub>-C<sub>4</sub>-alkoxy or by di(C<sub>1</sub>-C<sub>4</sub>-alkyl)amino, or is cyclohexyl;

(A13) The compounds claimed in European Patent 70,386, preferably those of the formula (XIV)



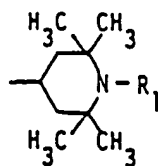
40 in which R<sub>1</sub> is allyloxy, allylamino or diallylamino, R<sub>2</sub> is C<sub>1</sub>-C<sub>4</sub>-alkoxy, allyloxy, allylamino, diallylamino, C<sub>1</sub>-C<sub>8</sub>-alkylamino, C<sub>2</sub>-C<sub>8</sub>-dialkylamino, morpholino or a group



R<sub>3</sub> is hydrogen or methyl, R<sub>5</sub> is hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl or a group

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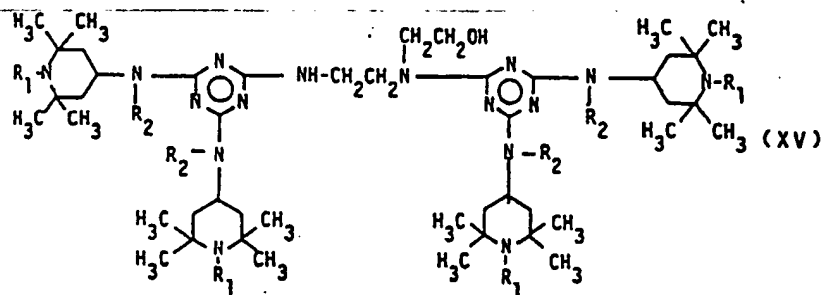




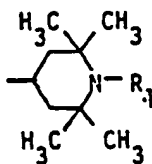
and  $R_4$  is  $C_2$ - $C_6$ -alkylene;

(A14) The polymers claimed in US Patents 4,413,093 and 4,435,555, obtained from compounds of the formula (XIV);

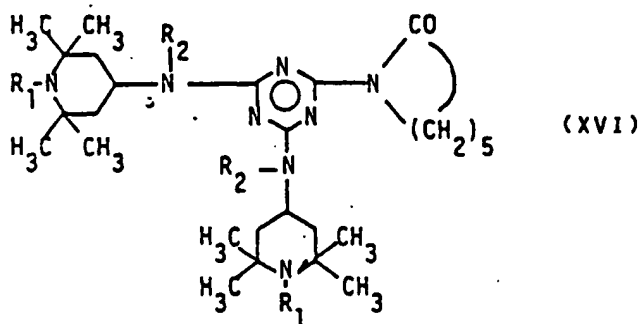
(A15) The compounds claimed in European Patent 72,009, preferably those of the formula (XV)

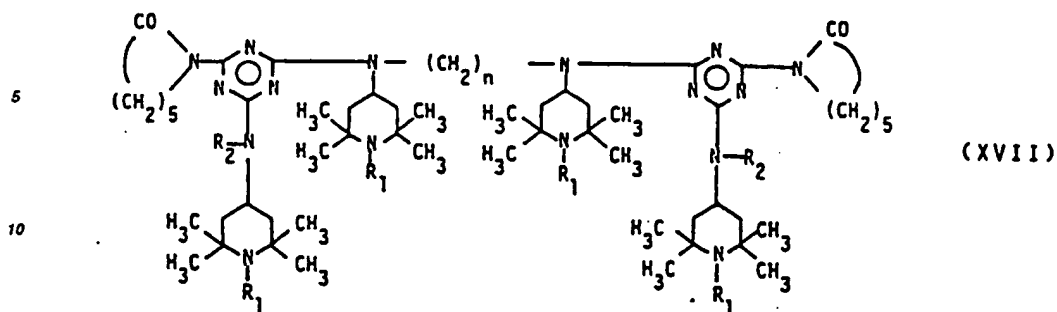


in which  $R_1$  is hydrogen or methyl,  $R_2$  is hydrogen,  $C_1$ - $C_6$ -alkyl,  $(C_1$ - $C_4$ )-alkoxypropyl, dimethylaminopropyl, diethylaminopropyl, cyclohexyl or a group

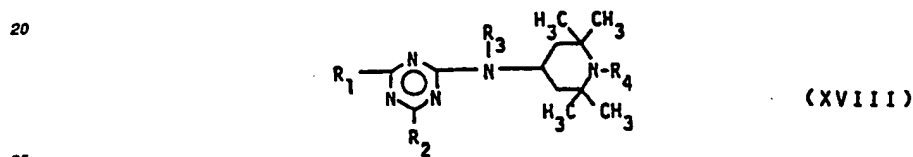


(A16) The compounds claimed in European Patent 75,849, preferably those of the formulae (XVI) and (XVII)





15 in which  $R_1$  is hydrogen or methyl,  $R_2$  is hydrogen,  $C_1$ - $C_8$ -alkyl, cyclohexyl,  $C_2$ - $C_4$ -alkyl substituted by OH,  $C_1$ - $C_4$ -alkoxy, dimethylamino or diethylamino, and  $n$  is a number from 2 to 6;  
 (A17) The compounds claimed in European Patent 82,244, preferably those of the formula (XVIII)



in which  $R_1$  is allyloxy, allylamino or diallylamino,  $R_2$  is the same as  $R_1$  or is  $C_1$ - $C_8$ -alkylamino, di( $C_1$ - $C_4$ -alkyl)-amino, morpholino or a group



$R_3$  is hydrogen,  $C_1$ - $C_8$ -alkyl or a group

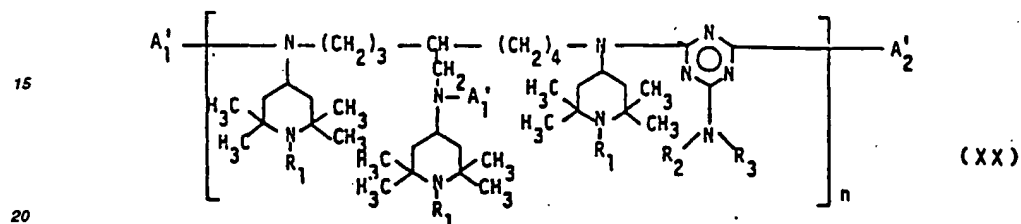
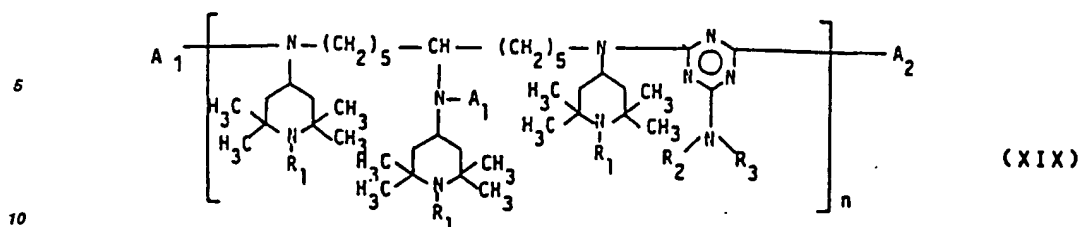


and  $R_4$  is hydrogen or methyl;

(A18) The compounds claimed in European Patent 94,048, preferably those of the formulae (XIX) and (XX)

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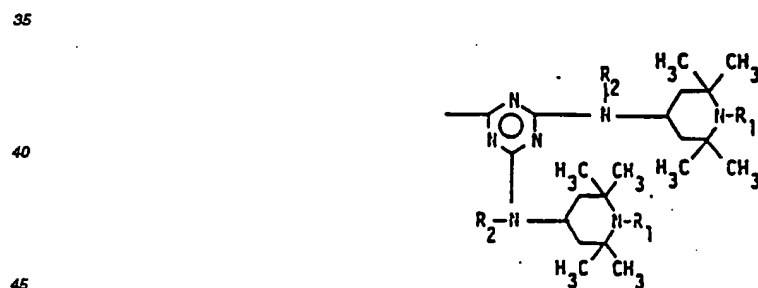
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in which n is a number from 1 to 10, R<sub>1</sub> is hydrogen or methyl, R<sub>2</sub> and R<sub>3</sub> which can be identical or different are C<sub>1</sub>-C<sub>8</sub>-alkyl or a group



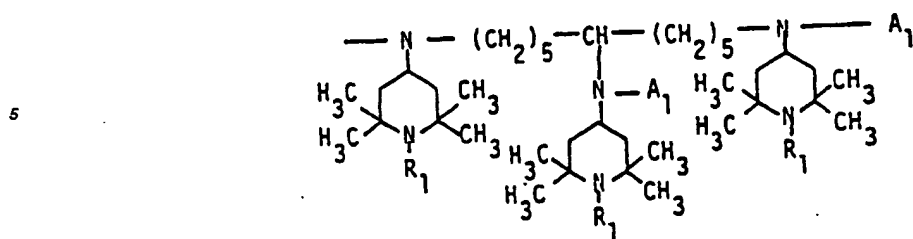
**A<sub>1</sub> and A'<sub>1</sub> are hydrogen or a group**



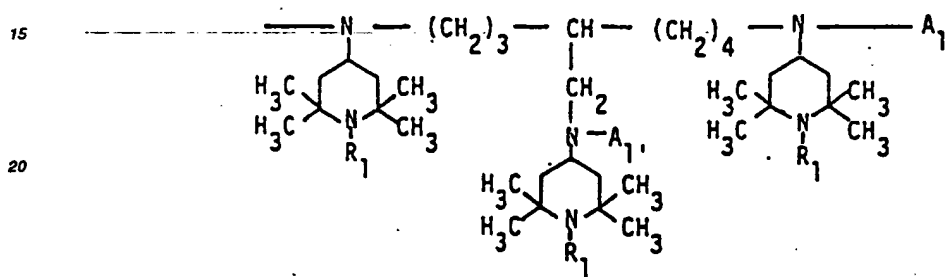
and  $A_2$  and  $A'_2$  are a group



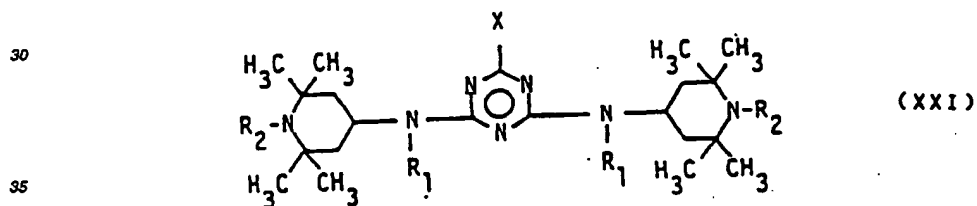
or  $A_2$  is a group



and A<sub>2</sub>' is a group



(A19) The compounds claimed in European Patent 107,615, preferably those of the formula (XXI)



in which R<sub>1</sub> is C<sub>1</sub>-C<sub>8</sub>-alkyl, cyclohexyl, benzyl or C<sub>2</sub>-C<sub>4</sub>-alkyl substituted by C<sub>1</sub>-C<sub>4</sub>-alkoxy or dimethylamino or diethylamino, R<sub>2</sub> is hydrogen or methyl, X is morpholino or a group

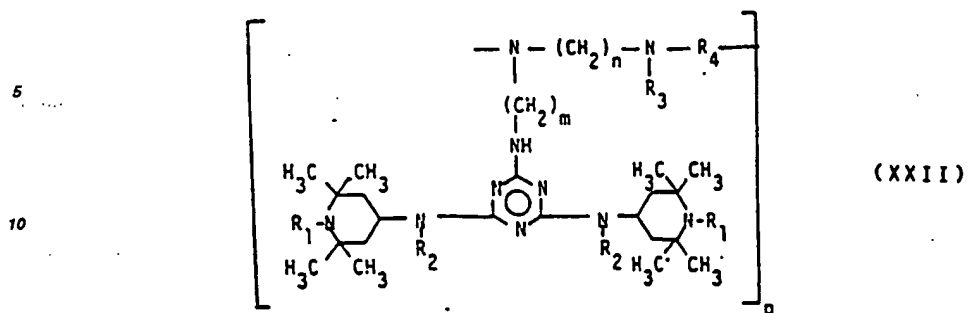


-OR<sub>5</sub> or a group

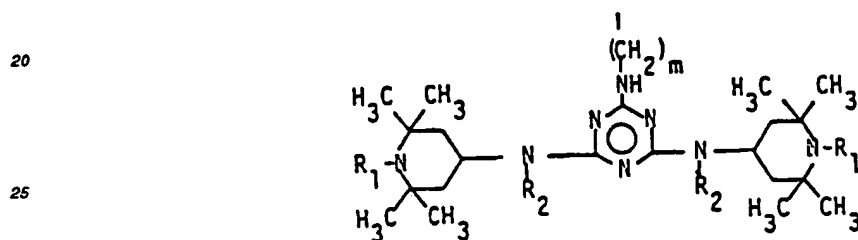


55 where R<sub>3</sub> and R<sub>4</sub> which can be identical or different are C<sub>1</sub>-C<sub>8</sub>-alkyl, cyclohexyl, benzyl or C<sub>2</sub>-C<sub>4</sub>-alkyl substituted by OH, C<sub>1</sub>-C<sub>4</sub>-alkoxy, dimethylamino or diethylamino, R<sub>4</sub> can also be hydrogen and R<sub>5</sub> is C<sub>1</sub>-C<sub>8</sub>-alkyl, allyl, cyclohexyl or benzyl;

(A20) The compounds claimed in US Patent 4,477,615, preferably those of the formula (XXII)



15 in which m and n which can be identical or different are numbers from 2 to 6; p is a number from 2 to 20, R<sub>1</sub> is hydrogen or methyl, R<sub>2</sub> is hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, cyclohexyl or benzyl, R<sub>3</sub> is hydrogen or a group of the formula



30 R<sub>4</sub> is C<sub>2</sub>-C<sub>6</sub>-alkylene, xylylene, 2-hydroxytrimethylene or a group of the formula



40 where R<sub>5</sub> is C<sub>1</sub>-C<sub>8</sub>-alkoxy, phenoxy, C<sub>1</sub>-C<sub>8</sub>-alkylamino, di(C<sub>1</sub>-C<sub>4</sub>-alkyl)amino, cyclohexylamino, morpholino or a group



50 (A21) The compounds claimed in US Patent 4,533,688, preferably those of the formula (XXIII)

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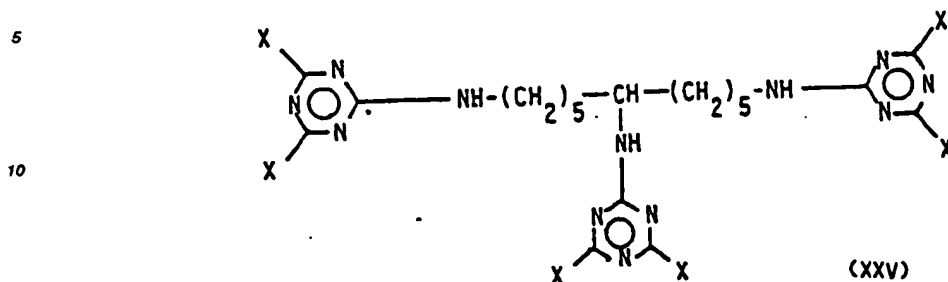
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molecular weight between 800 and 5,000;

(A23) The compounds claimed in European Patent 176,106, preferably those of the formula (XXV)



in which X is a group

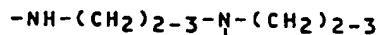


where  $R_1$  is hydrogen or methyl and  $R_2$  is hydrogen or  $C_1$ - $C_8$ -alkyl.

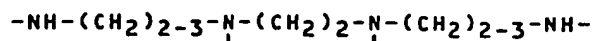
Preferred compounds (A) are those of the formulae (II), (III), (IV), (V), (X) and (XXI).

30 Particularly preferred compounds (A) are those of the formula (II) in which  $R_1$  is  $C_2$ - $C_8$ -alkyl or cyclohexyl,  $R_2$  is hydrogen or  $C_2$ - $C_8$ -alkyl,  $R_3$  is hydrogen or methyl,  $R_4$  is  $-(CH_2)_{2-6}$  and  $n$  is a number from 2 to 10, those of the formula (III) in which  $R_1$  is hydrogen or methyl,  $R_2$  is  $-(CH_2)_6$ ,  $R_3$  is  $-(CH_2)_{2-6}$  and  $n$  is a number from 2 to 10, those of the formula (IV) in which  $R_1$  is hydrogen or methyl,  $R_2$  is  $C_1$ - $C_4$ -alkyl,  $n$  is 2, 3 or 4 and  $R_3$  is a group of the formula  $-NH$   $(CH_2)_{2-6}NH$ - for  $n = 2$ ,

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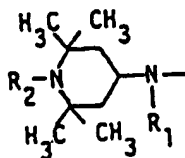


40  $NH$ - for  $n = 3$  and



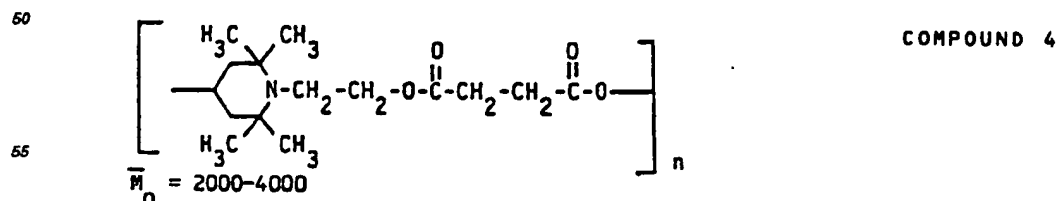
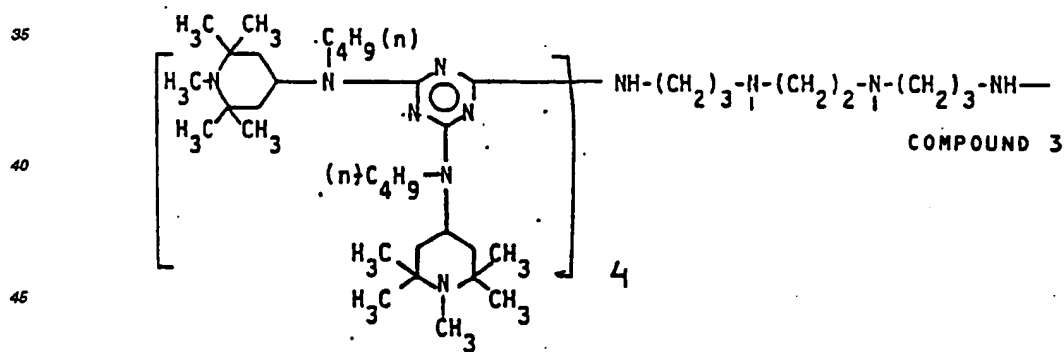
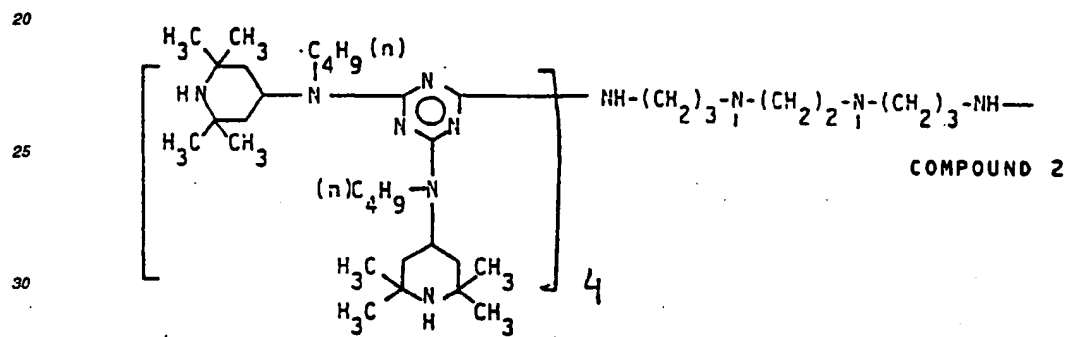
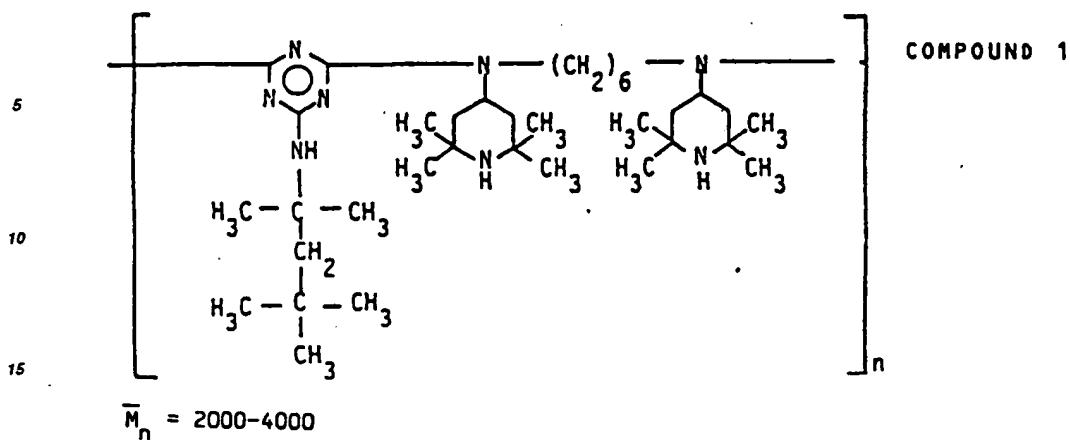
45 for  $n = 4$ , those of the formula (V) in which  $R$  is  $-(CH_2)_{2-6}$  and  $n$  is a number from 2 to 20, those of the formula (X) in which  $R_1$  is hydrogen or methyl,  $R_2$  is  $-(CH_2)_{2-6}$  and  $n$  is a number from 2 to 10, and those of the formula (XXI) in which  $R_1$  is  $C_1$ - $C_8$ -alkyl,  $R_2$  is hydrogen or methyl and X is a group

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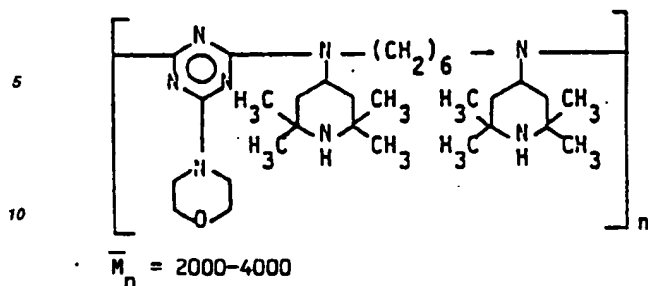


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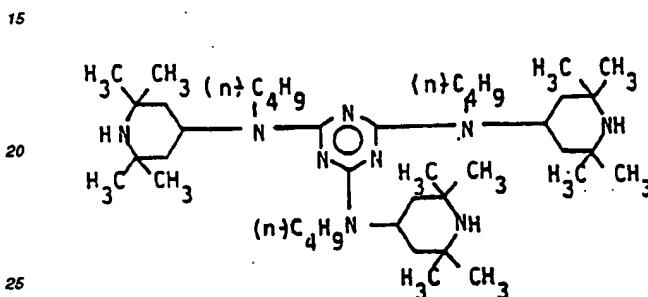
Compounds (A) of particular interest are:







COMPOUND 5



COMPOUND 6

The said compounds can be used by themselves or as a mixture with one another.

Compounds (B) which can be used according to the present invention are preferably the oxides and hydroxides of Mg and Zn.

The oxides of Mg and Zn are particularly preferred, and they can be used by themselves or as a mixture with one another.

The compounds (C) which can be used according to the present invention, if desired, are preferably salts of Al, Ca, Mg and Zn with  $C_{12}$ - $C_{18}$ -carboxylic acids.

The stearates of Ca, Mg and Zn, which can be used by themselves or as a mixture with one another, are particularly preferred.

The percentages by weight, relative to the weight of the polyethylene, of compounds (A), (B) and (C) are: 0.025 to 2%, preferably 0.05 to 1%, for compounds (A), 0.005 to 1%, preferably 0.025 to 0.5%, for compounds (B) and 0.005 to 1%, preferably 0.025 to 0.5%, for compounds (C).

The compounds (A), (B) and (C) can be mixed with one another before they are added to the polymer, or they can be added separately to the polymer, using any one of the known processes.

If desired, other additives conventional for polyethylene, such as phenolic antioxidants, phosphites, UV absorbers and other types of light stabilizers, can be added to the compounds (A), (B) and (C) of the present invention.

Examples of additives which can be mixed with the compounds (A) (B) and (C) are:

Phenolic antioxidants from the following classes:

Alkylated monophenols, for example 2,6-di-t-butyl-4-methyl-phenol, 2-t-butyl-4,6-dimethylphenol, 2,6-di-t-butyl-4-ethyl-phenol, 2,6-di-t-butyl-4-n-butylphenol, 2,6-di-t-butyl-4-isobutylphenol, 2,6-di-cyclopentyl-4-methylphenol, 2-( $\alpha$ -methyl-cyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-t-butyl-4-methoxymethylphenol and 2,6-dinonyl-4-methylphenol.

Alkylated hydroquinones, for example 2,6-di-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone, 2,5-di-t-amylhydroquinone and 2,6-diphenyl-4-octadecyloxyphenol.

Thiobisphenols, for example 2,2'-thio-bis-(6-t-butyl-4-methylphenol), 2,2'-thio-bis-(4-octylphenol), 4,4'-thio-bis-(6-t-butyl-3-methylphenol) and 4,4'-thio-bis-(6-t-butyl-2-methylphenol).

Alkylidene-bisphenols, for example 2,2'-methylene-bis-(6-t-butyl-4-methylphenol), 2,2'-methylene-bis-(6-t-butyl-4-ethylphenol), 2,2'-methylene-bis-(4-methyl-6-( $\alpha$ -methylcyclohexyl)-phenol), 2,2'-methylene-bis-(4-methyl-6-cyclohexylphenol), 2,2'-methylene-bis-(6-nonyl-4-methylphenol), 2,2'-methylene-bis-(4,6-di-t-butylphenol), 2,2'-ethyl-

dene-bis-(4,6-di-t-butylphenol), 2,2'-ethylidene-bis-(6-t-butyl-4-isobutylphenol), 2,2'-methylene-bis-[6-( $\alpha$ -methylbenzyl)-4-nonylphenol], 2,2'-methylene-bis-(6-( $\alpha$ , $\alpha$ -dimethylbenzyl)-4-nonylphenol), 4,4'-methylene-bis-(2,6-di-t-butylphenol), 4,4'-methylene-bis-(6-t-butyl-2-methylphenol), 1,1-bis-(5-t-butyl-4-hydroxy-2-methylphenyl)-butane, 2,6-bis-(3-t-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris-(5-t-butyl-4-hydroxy-2-methylphenyl)-butane, 1,1-bis-(5-t-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis-C3,3-bis-(3'-t-butyl-4'-hydroxyphenyl)-butyrate, bis-(3-t-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene and bis-[2-(3'-t-butyl-2'-hydroxy-5'-methylbenzyl)-6-t-butyl-4-methylphenyl] terephthalate.

Benzyl compounds, for example 1,3,5-tris-(3,5-di-t-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, bis-(3,5-di-t-butyl-4-hydroxybenzyl) sulfide, isooctyl 3,5-di-t-butyl-4-hydroxybenzyl-mercaptoacetate, bis-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) dithiolterephthalate, 1,3,5-tris-(3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, dioctadecyl 3,5-di-t-butyl-4-hydroxybenzylphosphonate, calcium monoethyl 3,5-di-t-butyl-4-hydroxybenzylphosphonate and 1,3,5-tris-(3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate.

Acylaminophenols, for example lauric acid 4-hydroxyanilide, stearic acid 4-hydroxyanilide, 2,4-bis-(octylmercapto)-6-(3,5-di-t-butyl-4-hydroxyanilino)-s-triazine and octyl N-(3,5-di-t-butyl-4-hydroxyphenyl)-carbamate.

Esters of  $\beta$ -(3,5-di-t-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, for example methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris-(hydroxyethyl) isocyanurate, thiodiethylene glycol and N,N'-bis-(hydroxyethyl)-oxamide.

Esters of  $\beta$ -(5-t-butyl-4-hydroxy-3-methylphenyl)-propionic acid with monohydric or polyhydric alcohols, for example methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris-(hydroxyethyl) isocyanurate, thiodiethylene glycol and N,N'-bis-(hydroxyethyl)-oxamide.

Esters of  $\beta$ -(3,5-dicyclohexyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, for example methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris-(hydroxyethyl) isocyanurate, thiodiethylene glycol and N,N'-bis-(hydroxyethyl)-oxamide.

Amides of  $\beta$ -(3,5-di-t-butyl-4-hydroxyphenyl)-propionic acid, for example N,N'-bis-(3,5-di-t-butyl-4-hydroxyphenyl)-propionyl--hexamethylenediamine, N,N'-bis-(3,5-di-t-butyl-4-hydroxyphenyl)-propionyl--trimethylenediamine and N,N'-bis-(3,5-di-t-butyl-4-hydroxyphenyl)-propionyl--hydrazine.

#### UV absorbers and light stabilizers

2-(2'-Hydroxyphenyl)-benzotriazoles, for example the 5'-methyl, 3',5'-di-t-butyl, 5'-t-butyl, 5'-(1,1,3,3-tetramethylbutyl), 5-chloro-3',5'-di-t-butyl, 5-chloro-3'-t-butyl-5'-methyl, 3'-sec.-butyl-5'-t-butyl, 4'-octoxy-3',5'-di-t-amyl and 3',5'-bis-( $\alpha$ , $\alpha$ -dimethylbenzyl) derivatives.

2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octoxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

Esters of various substituted benzoic acids, for example 4-t-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis-(4-t-butylbenzoyl)-resorcinol, benzoylresorcinol, 2,4-di-t-butylphenyl 3,5-di-t-butyl-4-hydroxybenzoate and hexadecyl 3,5-di-t-butyl-4-hydroxybenzoate.

Acrylates, for example ethyl  $\alpha$ -cyano- $\beta$ , $\beta$ -diphenyl-acrylate, isooctyl  $\alpha$ -cyano- $\beta$ , $\beta$ -diphenylacrylate, methyl  $\alpha$ -carbomethoxycinnamate, methyl  $\alpha$ -cyano- $\beta$ -methyl-p-methoxycinnamate, butyl  $\alpha$ -cyano- $\beta$ -methyl-p-methoxycinnamate, methyl  $\alpha$ -carbomethoxy-p-methoxycinnamate and N-( $\beta$ -carbomethoxy- $\beta$ -cyanovinyl)-2-methyl-indoline.

Nickel compounds, for example nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3-bis-(4-(1,1,3,3-tetramethylbutyl)-phenol)], such as the 1:1 or 1:2 complexes, which may contain additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of monoalkyl esters of 4-hydroxy-3,5-di-t-butylbenzylphosphonic acid, such as the methyl or ethyl esters, nickel complexes of ketoximes such as 2-hydroxy-4-methylphenyl undecyl ketoxime and nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

Oxalic acid diamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-di-t-butylloxanilide, 2,2'-didodecyloxy-5,5'-di-t-butylloxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis-(3-dimethylaminopropyl)-oxamide, 2-ethoxy-5-t-butyl-2'-ethyloxanilide and its mixtures with 2-ethoxy-2'-ethyl-5,4'-di-t-butylloxanilide, and mixtures of ortho- and paramethoxy and also o- and p-ethoxy-disubstituted oxanilides.

Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris-(nonylphenyl) phosphite, triauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris-(2,4-di-t-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis-(2,4-di-t-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis-(2,4-di-t-butylphenyl) 4,4'-diphenylenediphosphonite and 3,9-bis-(2,4-di-t-butylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane.

The use of the stabilizer mixtures according to the present invention is illustrated by the examples which follow; these are given by way of illustration only and do not imply any restriction.

**EXAMPLES 1 - 10**

10 kg of low-density polyethylene powder of melt index 0.6 (Fertene EF 3-2000, a product from Soc. Enichem Polimeri) are mixed in a slow mixer with the compounds indicated in Table 1.

The mixtures are then extruded at a temperature of 190°C and converted into granules, from which stretched films of 150 µm thickness are obtained by blow extrusion using a Dolci pilot extruder (screw diameter = 45/26 D and head diameter = 100 mm) under the following working conditions:

body temperature = 170-190-200°C

head temperature = 200-200-200-190°C

The films obtained are exposed outdoors at 45°, facing south, on pinewood at Pontecchio Marconi (Bologna) (about 110 kly/year). The residual elongation is measured on samples, taken after various times of exposure by means of a constant-speed tensometer.

The energy received (expressed in kilolangley) needed to halve the initial elongation value is then calculated ( $T_{50}$ ). The results obtained are shown in Table 1.

TABLE 1

Example No.	Compound A (g)	Compound B (g)	Compound C (g)	$T_{50}$ elongation (kly)
1	Compound 1 (20)	-	-	117
2	•	MgO (10)	-	168
3	•	ZnO (10)	-	138
4	•	MgO (10)	Ca stearate (10)	193
5	•	ZnO (10)	•	161
6	Compound 2 (20)	-	-	128
7	•	MgO (10)	-	175
8	•	ZnO (10)	-	154
9	•	MgO (10)	Ca stearate (10)	192
10	•	ZnO (10)	•	186

**Examples 11-18**

10 kg of low-density polyethylene powder of melt index 0.1 (Fertene EF 3-2000, a product from Soc. ENICHEM POLIMERI) are mixed in a slow mixer with the compounds indicated in Table 2.

The mixtures are then extruded at a temperature of 190°C and converted into granules, from which stretched films of 150 µm thickness are obtained by blow extrusion using a Dolci pilot extruder (screw diameter = 45/26D and head diameter = 100 mm) under the following working conditions:

body temperature = 170 - 190 - 200°C

head temperature = 200 - 200 - 200 - 190°C

The films obtained are exposed in a model 65 WR Weather - O-meter (ASTM G 26 - 77) with a black panel temperature of 63°C. The residual elongation is measured on samples, taken after various times of exposure to light, by means of a constant speed tensometer; the exposure time in hours ( $T_{50}$ ) needed to halve the initial elongation value is then calculated. The results obtained are shown in Table 2:

Table 2

Example N°	Compound A (g)	Compound B (g)	Compound C (g)	$T_{50}$ (hours)
11	compound 1 (10)	-	-	3900
12	"	ZnO (5)	Ca stearate (5)	> 4500
13	compound 3 (10)	-	-	3600
14	"	ZnO (5)	Ca stearate (5)	> 4500
15	compound 5 (10)	-	-	3140
16	"	ZnO (5)	Ca stearate (5)	4100
17	compound 6 (10)	-	-	3040
18	"	ZnO (5)	Ca stearate (5)	> 4500

#### Examples 19-21

10 kg of linear low-density polyethylene (LLDPE) powder of melt index 0.9 (Dowlex 2045, a product from Dow Chemical) are mixed in a slow mixer with 2 g of pentaerythritol-tetrakis [3-(3,5-di-*t*-butyl-4-hydroxy-phenyl)propionate], 8 g of tris-(2,4-di-*t*-butyl-phenyl)phosphite and with the compounds indicated in Table 3.

The mixtures are then extruded to give stretched films of 150  $\mu$ m thickness by blow extrusion using a Dolci pilot extruder (screw diameter = 45/26D and head diameter = 100 mm) under the following working conditions:

body temperature: 180 - 220 - 220°C

head temperature: 220 - 220 - 220 - 220°C

The films obtained are exposed outdoors at 45°, facing south, on pinewood at Pontecchio Marconi (Bologna) (about 110 kly/ year). The residual elongation is measured on samples, taken after various times of exposure by means of a constant speed tensometer.

The energy received (express in Kilolangleys) needed to halve the initial elongation value is then calculated ( $T_{50}$ ). The results obtained are shown in Table 3.

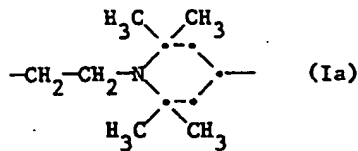
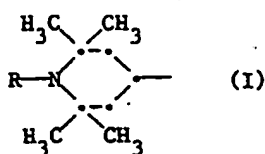
Table 3

Example No.	Compound A (g)	Compound B (g)	Compound C (g)	$T_{50}$ elongation (Klys)
19	compound 1 (30)	-	-	98
20	"	MgO (10)	-	135
21	"	ZnO (10)	-	127

## Claims

1. A light stabilizer composition for polyethylene, comprising:

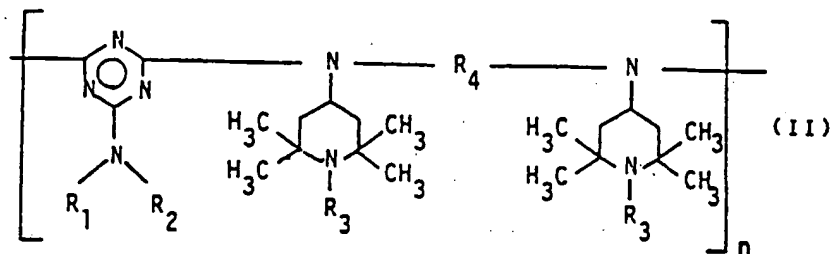
(A) one or more compounds with piperidine groups of the formula (I) or (Ia)



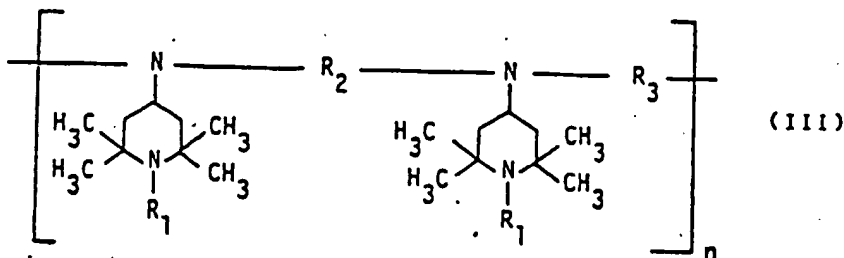
in which R is hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkyl, allyl, benzyl, acetyl, acryloyl, 2-hydroxyethyl or 2-hydroxypropyl, said piperidine group of formula (I) not being bound in the 4-position to an oxygen atom, and  
(B) one or more metal compounds selected from an oxide or hydroxide of Al, Mg and Zn.

2. A light stabilizer composition for polyethylene, comprising, in addition to compounds (A) and (B) of claim 1:  
(C) one or more salts of Al, Ba, Ca, Mg, Sr and Zn with a C<sub>1</sub>-C<sub>22</sub>-carboxylic acid.

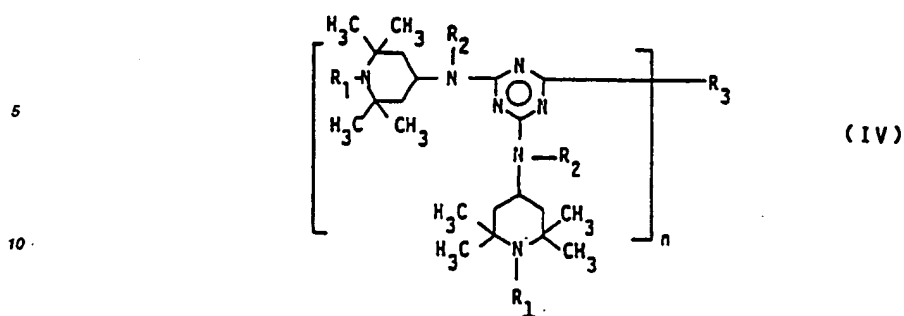
3. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formulae



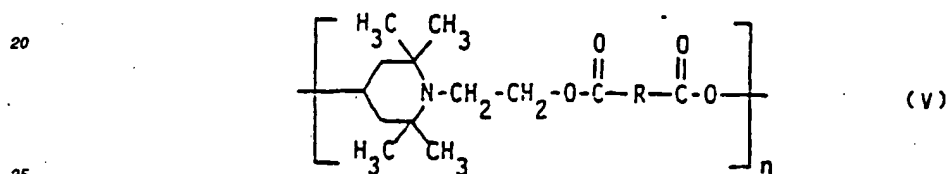
in which R<sub>1</sub> is C<sub>1</sub>-C<sub>8</sub>-alkyl, cyclohexyl, 2,2,6,6-tetramethyl-(piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, R<sub>2</sub> is hydrogen or C<sub>1</sub>-C<sub>8</sub>-alkyl, R<sub>3</sub> is hydrogen or methyl, R<sub>4</sub> is C<sub>2</sub>-C<sub>6</sub>-alkylene and n is a number from 2 to 20;



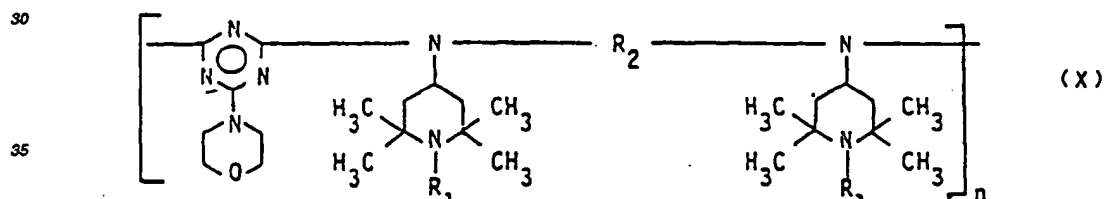
in which R<sub>1</sub> is hydrogen or methyl, R<sub>2</sub> is C<sub>2</sub>-C<sub>6</sub>-alkylene, R<sub>3</sub> is C<sub>2</sub>-C<sub>6</sub>-alkylene, 2-hydroxytrimethylene or xylylene and n is a number from 2 to 20;



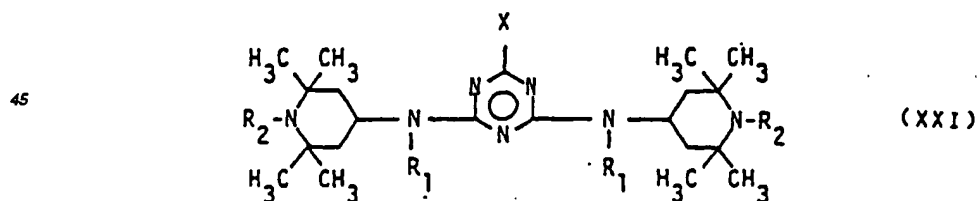
in which  $R_1$  is hydrogen or methyl,  $R_2$  is hydrogen,  $C_1$ - $C_8$ -alkyl, cyclohexyl, 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl,  $n$  is 2, 3 or 4 and  $R_3$  is the radical of an  $n$ -valent polyamine;



in which  $R$  is  $C_2$ - $C_8$ -alkylene and  $n$  is a number from 2 to 30;



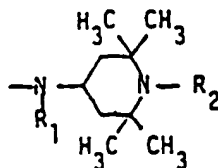
in which  $R_1$  is hydrogen or methyl,  $R_2$  is  $C_2$ - $C_6$ -alkylene and  $n$  is a number from 2 to 20; and



in which  $R_1$  is  $C_1$ - $C_8$ -alkyl, cyclohexyl, benzyl or  $C_2$ - $C_4$ -alkyl substituted by  $C_1$ - $C_4$ -alkoxy or dimethylamino or diethylamino,  $R_2$  is hydrogen or methyl,  $X$  is morpholino or a group



$-\text{OR}_5$  or a group

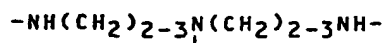


where  $R_3$  and  $R_4$  which can be identical or different are  $C_1$ - $C_8$ -alkyl, cyclohexyl, benzyl or  $C_2$ - $C_4$ -alkyl substituted by OH,  $C_1$ - $C_4$ -alkoxy, dimethylamino or diethylamino,  $R_4$  can also be hydrogen and  $R_5$  is  $C_1$ - $C_8$ -alkyl, allyl, cyclohexyl or benzyl.

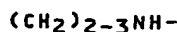
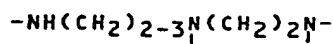
4. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising compounds of the formula (II) in which  $R_1$  is  $C_2$ - $C_8$ -alkyl or cyclohexyl,  $R_2$  is hydrogen or  $C_2$ - $C_8$ -alkyl,  $R_3$  is hydrogen or methyl,  $R_4$  is  $(CH_2)_{2-6}$ - and  $n$  is a number from 2 to 10.

5. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formula (III) in which  $R_1$  is hydrogen or methyl,  $R_2$  is  $-(CH_2)_6$ -,  $R_3$  is  $-(CH_2)_{2-6}$ - and  $n$  is a number from 2 to 10.

6. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formula (IV), in which  $R_1$  is hydrogen or methyl,  $R_2$  is  $C_1$ - $C_4$ -alkyl,  $n$  is 2, 3 or 4, and  $R_3$  is a group of the formula  $-NH(CH_2)_{2-6}NH-$  for  $n = 2$ ,



for  $n = 3$  and

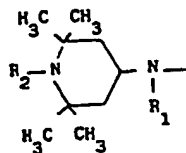


for  $n = 4$ .

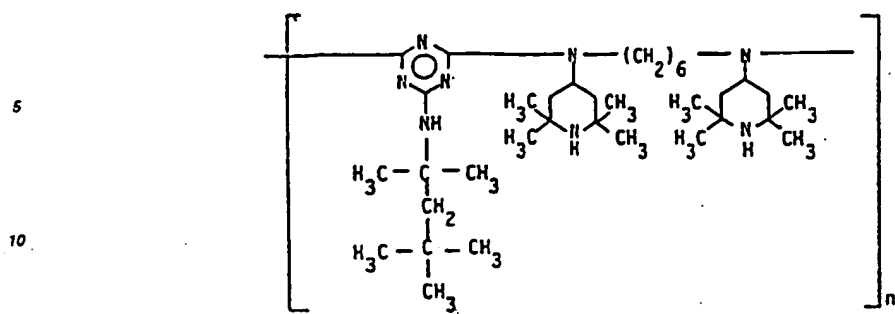
7. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formula (V), in which  $R$  is  $-(CH_2)_{2-6}$ - and  $n$  is a number from 2 to 20.

8. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formula (X), in which  $R_1$  is hydrogen or methyl,  $R_2$  is  $-(CH_2)_{2-6}$ - and  $n$  is a number from 2 to 10.

9. A light stabilizer composition according to claim 1, wherein the compound (A) is selected from the group comprising the compounds of the formula (XXI), in which  $R_1$  is  $C_1$ - $C_8$ -alkyl,  $R_2$  is hydrogen or methyl and  $X$  is a group



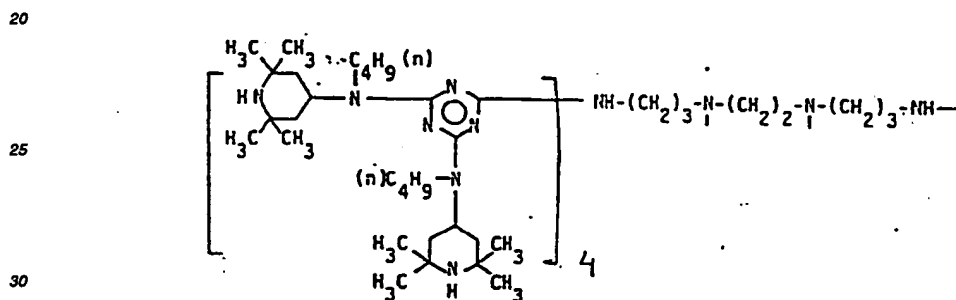
10. A light stabilizer composition according to claim 1, wherein the compound (A) is that of the formula



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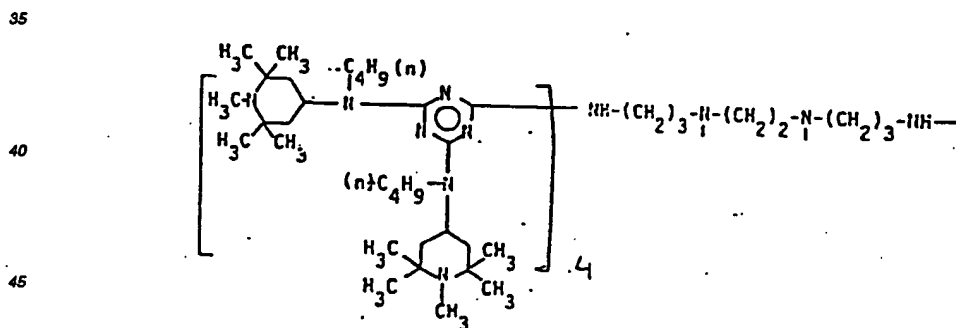
of a molecular weight between 2,000 and 4,000.

**11. A light stabilizer composition according to claim 1, wherein the compound (A) is that of the formula**



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**12. A light stabilizer composition according to claim 1, wherein the compound (A) is that of the formula**



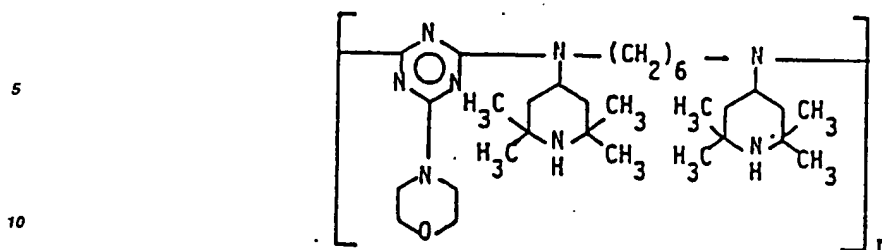
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**13. A light stabilizer composition according to claim 1, wherein the compound (A) is that of the formula**

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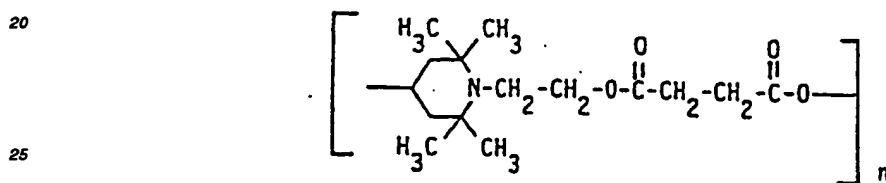
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15 of a molecular weight between 2,000 and 4,000.

14. A light stabilizer composition according to claim 1, wherein the compound (A) is that of the formula



of a molecular weight between 2,000 and 4,000.

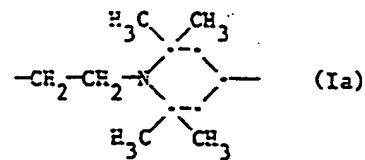
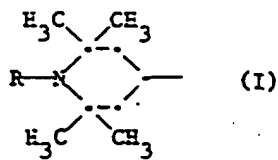
- 30 15. A light stabilizer composition according to claim 1, wherein the compound (B) is an oxide or hydroxide of Mg or Zn.
16. A light stabilizer composition according to claim 1, wherein the compound (B) is an oxide of Mg or Zn.
17. A light stabilizer composition according to claim 2, wherein the compound (C) is a salt of Al, Ca, Mg or Zn with C<sub>12</sub>-C<sub>18</sub>-carboxylic acid.
- 35 18. A light stabilizer composition according to claim 2, wherein the compound (C) is a salt of Ca, Mg or Zn with stearic acid.
- 40 19. Stabilized polyethylene containing a light stabilizer composition according to claim 1 or 2.
20. Stabilized polyethylene according to claim 19, wherein the percentages by weight, relative to the weight of the polyethylene, of compounds (A) and (B) are: 0.025 to 2%, preferably 0.05 to 1%, for compound (A) and 0.005 to 1%, preferably 0.025 to 0.5%, for compound (B).
- 45 21. Stabilized polyethylene according to claim 19, wherein the percentage by weight, relative to the polyethylene, of compound (C) is 0.005 to 1%, preferably 0.025 to 0.5%.
22. Stabilized polyethylene according to claim 19, which is low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) or a mixture thereof.
- 50 23. A film, prepared from low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) or a mixture thereof, stabilized with a light stabilizer composition of claim 1 or 2.

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# Patentansprüche

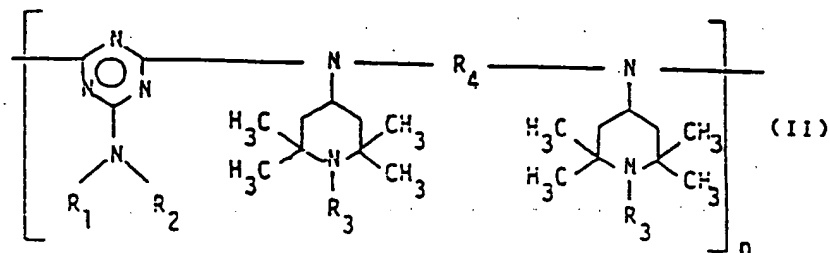
1. Lichtstabilisator-Zusammensetzung für Polyethylen, umfassend

(A) eine oder mehrere Verbindungen mit Piperidingruppen der Formel (I) oder (Ia)

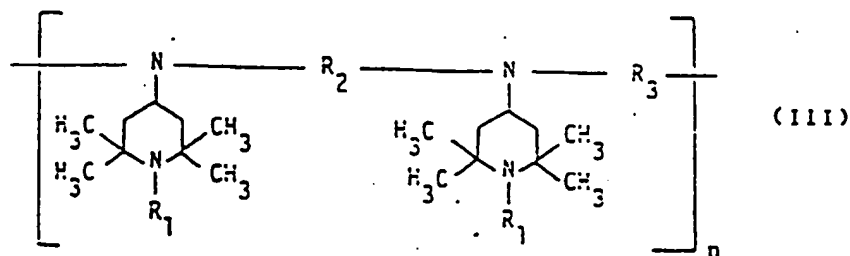


worin R Wasserstoff, C<sub>1-4</sub>-Alkyl, Allyl, Benzyl, Acetyl, Acryloyl, 2-Hydroxyethyl oder 2-Hydroxypropyl bedeutet, wobei die Piperidingruppe der Formel (I) nicht in 4-Stellung an ein Sauerstoffatom gebunden ist, und  
(B) eine oder mehrere Metallverbindungen, ausgewählt unter einem Oxid oder Hydroxid von Al, Mg und Zn.

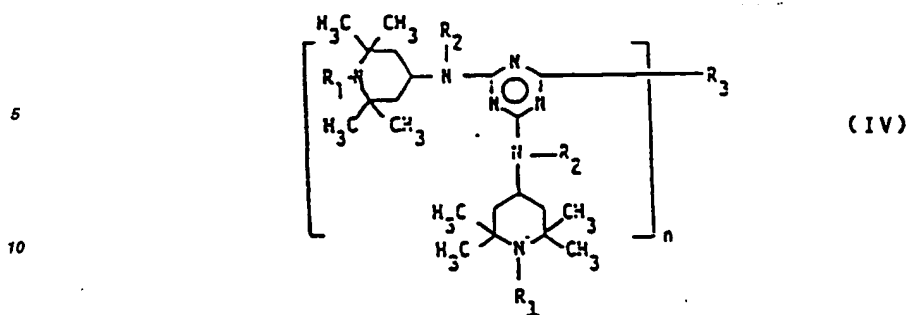
2. Lichtstabilisator-Zusammensetzung für Polyethylen, umfassend zusätzlich zu den Verbindungen (A) und (B) von Anspruch 1  
(C) ein oder mehrere Salze von Al, Ba, Ca, Mg, Sr und Zn mit einer C<sub>1-22</sub>-Carbonsäure.
3. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formeln



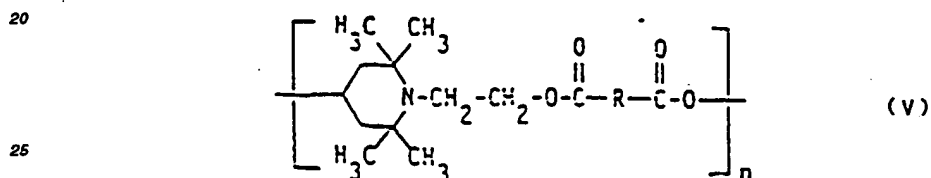
worin R<sub>1</sub> C<sub>1-8</sub>-Alkyl, Cyclohexyl, 2,2,6,6-Tetramethyl-4-piperidyl oder 1,2,2,6,6-Pentamethyl-4-piperidyl bedeutet, R<sub>2</sub> Wasserstoff oder C<sub>1-8</sub>-Alkyl ist, R<sub>3</sub> für Wasserstoff oder Methyl steht, R<sub>4</sub> für C<sub>2-6</sub>-Alkylen steht und n eine Zahl von 2 bis 20 ist;



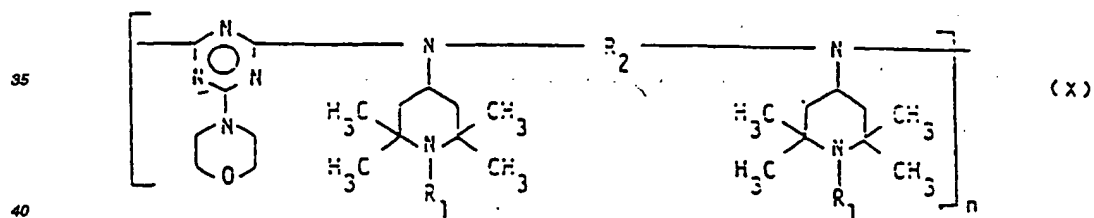
worin R<sub>1</sub> Wasserstoff oder Methyl bedeutet, R<sub>2</sub> C<sub>2-6</sub>-Alkylen ist, R<sub>3</sub> für C<sub>2-6</sub>-Alkylen, 2-Hydroxytrimethylen oder Xylylen steht und n eine Zahl von 2 bis 20 ist;



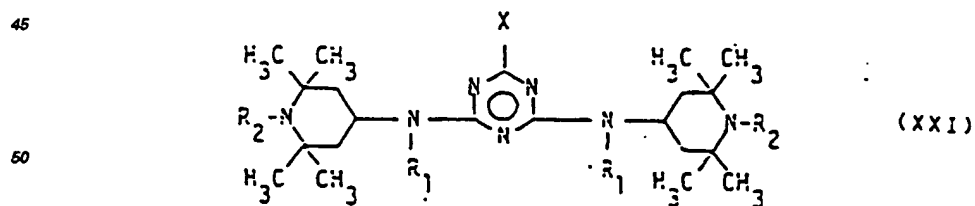
15 worin  $R_1$  Wasserstoff oder Methyl bedeutet,  $R_2$  Wasserstoff,  $C_{1-8}$ -Alkyl, Cyclohexyl, 2,2,6,6-Tetramethyl-4-piperidyl oder 1,2,2,6,6-Pentamethyl-4-piperidyl ist,  $n$  für 2, 3 oder 4 steht und  $R_3$  den Rest eines  $n$ -wertigen Polyamins wiedergibt;



30 worin  $R$   $C_{2-6}$ -Alkylen ist und  $n$  für eine Zahl von 2 bis 30 steht;



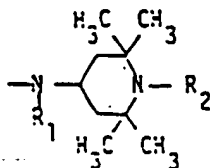
45 worin  $R_1$  Wasserstoff oder Methyl bedeutet,  $R_2$  für  $C_{2-6}$ -Alkylen steht und  $n$  eine Zahl von 2 bis 20 ist; und



60 worin  $R_1$   $C_{1-8}$ -Alkyl, Cyclohexyl, Benzyl oder  $C_{2-4}$ -Alkyl, substituiert durch  $C_{1-4}$ -Alkoxy oder Dimethylamino oder Diethylamino, ist,  $R_2$  für Wasserstoff oder Methyl steht,  $X$  Morpholino oder eine Gruppe

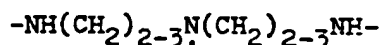


-OR<sub>5</sub> oder eine Gruppe

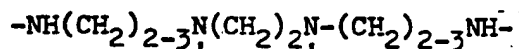


bedeutet, worin R<sub>3</sub> und R<sub>4</sub>, die identisch oder verschieden sein können, C<sub>1-8</sub>-Alkyl, Cyclohexyl, Benzyl oder C<sub>2-4</sub>-Alkyl, substituiert durch OH, C<sub>1-4</sub>-Alkoxy, Dimethylamino oder Diethylamino, sind, R<sub>4</sub> auch Wasserstoff sein kann und R<sub>5</sub> für C<sub>1-8</sub>-Alkyl, Allyl, Cyclohexyl oder Benzyl steht.

4. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (II), worin R<sub>1</sub> C<sub>2-8</sub>-Alkyl oder Cyclohexyl bedeutet, R<sub>2</sub> Wasserstoff oder C<sub>2-8</sub>-Alkyl ist, R<sub>3</sub> für Wasserstoff oder Methyl steht, R<sub>4</sub> für -(CH<sub>2</sub>)<sub>2-6</sub>- steht und n eine Zahl von 2 bis 10 ist.
5. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (III), worin R<sub>1</sub> Wasserstoff oder Methyl bedeutet, R<sub>2</sub> für -(CH<sub>2</sub>)<sub>6</sub>- steht, R<sub>3</sub> für -(CH<sub>2</sub>)<sub>2-6</sub>- steht und n eine Zahl von 2 bis 10 ist.
6. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (IV), worin R<sub>1</sub> Wasserstoff oder Methyl bedeutet, R<sub>2</sub> für C<sub>1-4</sub>-Alkyl steht, n für 2, 3 oder 4 steht und R<sub>3</sub> eine Gruppe der Formel -NH(CH<sub>2</sub>)<sub>2-6</sub>NH- für n = 2,

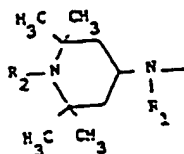


für n = 3 und



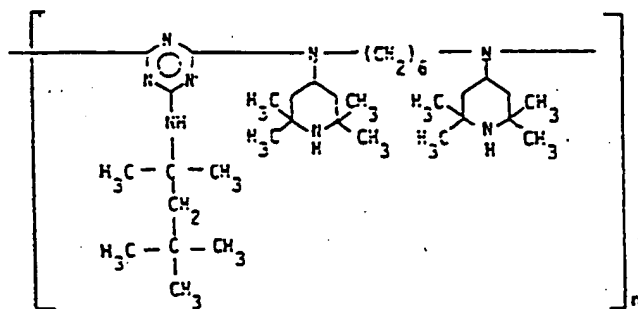
für n = 4 ist.

7. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (V), worin R für -(CH<sub>2</sub>)<sub>2-6</sub>- steht und n eine Zahl von 2 bis 20 ist.
8. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (X), worin R<sub>1</sub> Wasserstoff oder Methyl bedeutet, R<sub>2</sub> für -(CH<sub>2</sub>)<sub>2-6</sub>- steht und n eine Zahl von 2 bis 10 ist.
9. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) ausgewählt ist aus der Gruppe, umfassend die Verbindungen der Formel (XXI), worin R<sub>1</sub> C<sub>1-8</sub>-Alkyl ist, R<sub>2</sub> Wasserstoff oder Methyl bedeutet und X eine Gruppe



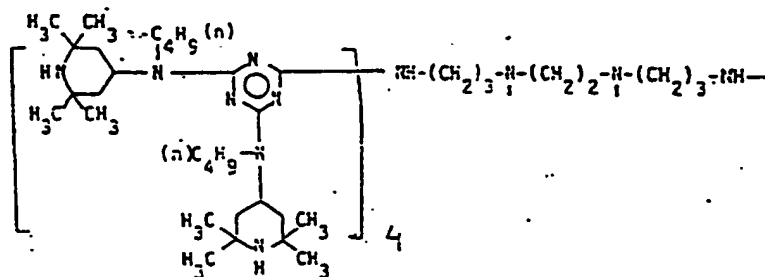
wiedergibt.

10. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) diejenige der Formel



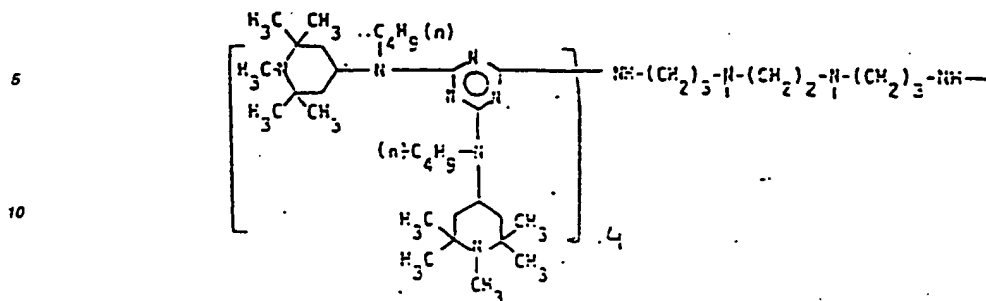
mit einem Molekulargewicht zwischen 2000 und 4000 ist.

11. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) diejenige der Formel



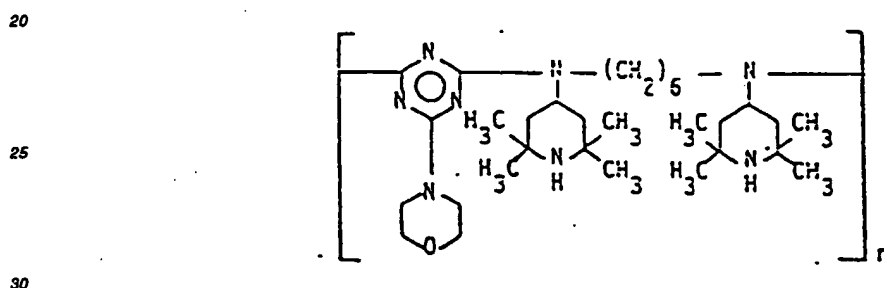
ist.

12. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) diejenige der Formel



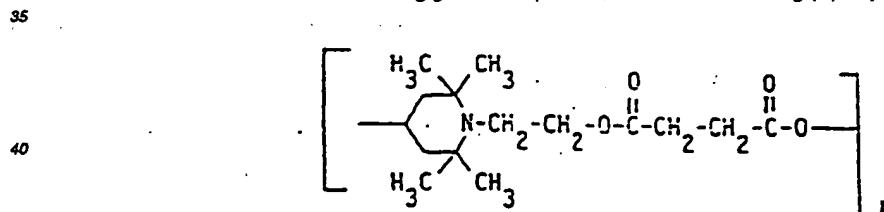
ist.

13. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) diejenige der Formel



mit einem Molekulargewicht zwischen 2000 und 4000 ist.

14. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (A) diejenige der Formel



mit einem Molekulargewicht zwischen 2000 und 4000 ist.

15. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (B) ein Oxid oder Hydroxid von Mg oder Zn ist.

16. Lichtstabilisator-Zusammensetzung gemäß Anspruch 1, worin die Verbindung (B) ein Oxid von Mg oder Zn ist.

17. Lichtstabilisator-Zusammensetzung gemäß Anspruch 2, worin die Verbindung (C) ein Salz von Al, Ca, Mg oder Zn mit einer C<sub>12-18</sub>-Carbonsäure ist.

18. Lichtstabilisator-Zusammensetzung gemäß Anspruch 2, worin die Verbindung (C) ein Salz von Ca, Mg oder Zn mit Stearinsäure ist.

19. Stabilisiertes Polyethylen, enthaltend eine Lichtstabilisator-Zusammensetzung gemäß Anspruch 1 oder 2.

20. Stabilisiertes Polyethylen gemäß Anspruch 19, worin die Gewichtsprozentanteile, bezogen auf das Gewicht des Polyethylens, der Verbindungen (A) und (B) sind: 0,025 bis 2%, bevorzugt 0,05 bis 1%, für Verbindung (A) und 0,005 bis 1%, bevorzugt 0,025 bis 0,5%, für Verbindung (B).
21. Stabilisiertes Polyethylen gemäß Anspruch 19, worin der Gewichtsprozentanteil, bezogen auf das Polyethylen, der Verbindung (C) 0,005 bis 1%, bevorzugt 0,025 bis 0,5%, beträgt.
22. Stabilisiertes Polyethylen gemäß Anspruch 19, bei dem es sich um Polyethylen niedriger Dichte (LDPE), lineares Polyethylen niedriger Dichte (LLDPE) oder eine Mischung hiervon handelt.
23. Film, hergestellt aus Polyethylen niedriger Dichte (LDPE), linearem Polyethylen niedriger Dichte (LLDPE) oder einer Mischung hiervon, stabilisiert mit einer Lichtstabilisator-Zusammensetzung gemäß Anspruch 1 oder 2.

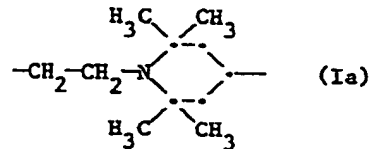
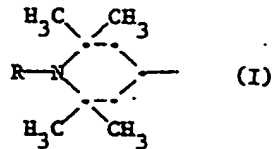
# Revendications

1. Composition de photostabilisants pour le polyéthylène comprenant

(A) un ou plusieurs composés comportant des groupes pipéridino de formule (I) ou (Ia)

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dans lesquelles R est l'hydrogène, alkyle en C<sub>1</sub>-C<sub>4</sub>, allyle, benzyle, acétyle, acryloyle, 2-hydroxyéthyle ou 2-hydroxypropyle, ledit groupe pipéridino de formule (I) n'étant pas lié en position 4 à un atome d'oxygène, et (B) un ou plusieurs composés métalliques pris parmi un oxyde ou un hydroxyde d'Al, de Mg et de Zn.

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2. Composition de photostabilisants pour le polyéthylène comprenant en plus des composés (A) et (B) de la revendication 1 :

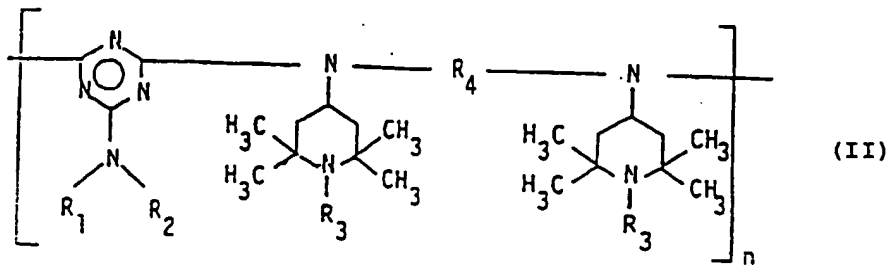
(C) un ou plusieurs sels d'Al, Ba, Ca, Mg, Sr et Zn avec un acide carboxylique en C<sub>1</sub>-C<sub>22</sub>.

3. Composition de photostabilisants selon la revendication 1, où le composé (A) est pris dans le groupe comprenant les composés de formules

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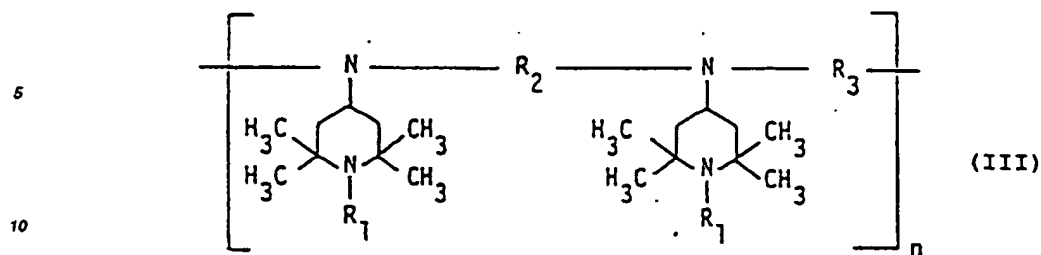
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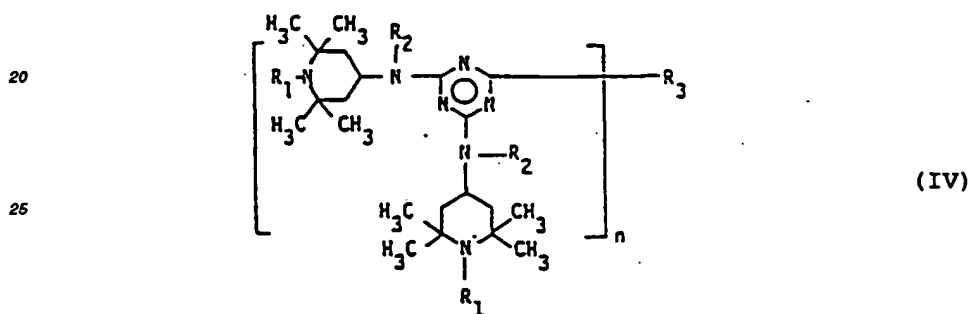


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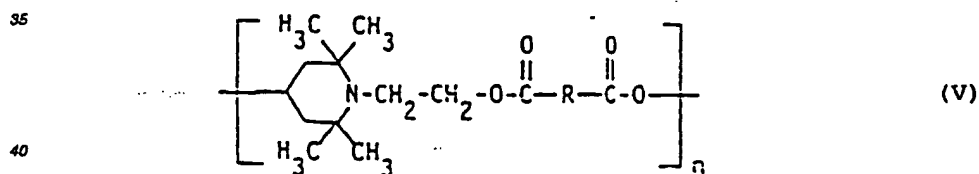
dans laquelle R<sub>1</sub> est alkyle en C<sub>1</sub>-C<sub>8</sub>, cyclohexyle, 2,2,6,6-tétraméthyl-4-pipéridyle ou 1,2,2,6,6-pentaméthyl-4-pipéridyle, R<sub>2</sub> est l'hydrogène ou alkyle en C<sub>1</sub>-C<sub>8</sub>, R<sub>3</sub> est l'hydrogène ou méthyle, R<sub>4</sub> est alkylène en C<sub>2</sub>-C<sub>8</sub> et n est un nombre de 2 à 20 ;



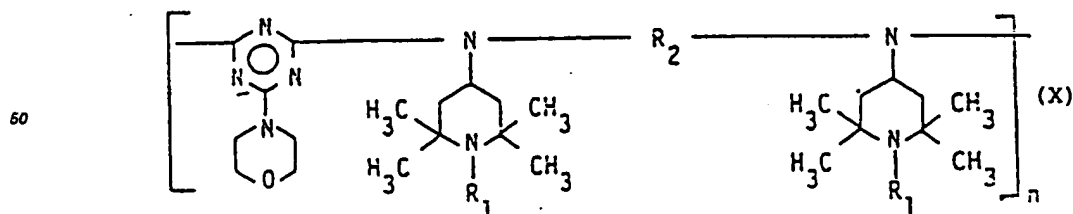
15 dans laquelle  $\text{R}_1$  est l'hydrogène ou méthyle,  $\text{R}_2$  est alkylène en  $\text{C}_2\text{-C}_6$ ,  $\text{R}_3$  est alkylène en  $\text{C}_2\text{-C}_6$ , 2-hydroxy-triméthylène ou xylène et  $n$  est un nombre de 2 à 20 ;



35 dans laquelle  $\text{R}_1$  est l'hydrogène ou méthyle,  $\text{R}_2$  est l'hydrogène, alkyle en  $\text{C}_1\text{-C}_6$ , cyclohexyle, 2,2,6,6-tétraméthyl-4-pipéridyle ou 1,2,2,6,6-pentaméthyl-4-pipéridyle,  $n$  vaut 2, 3 ou 4 et  $\text{R}_3$  est le radical  $n$ -valent d'une polyamine ;

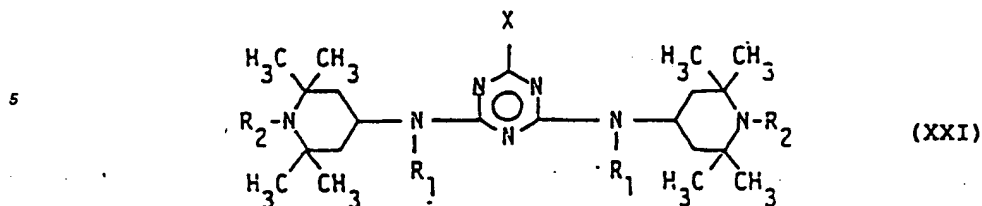


45 dans laquelle  $\text{R}$  est alkylène en  $\text{C}_2\text{-C}_8$  et  $n$  est un nombre de 2 à 30 ;



55 dans laquelle  $\text{R}_1$  est l'hydrogène ou méthyle,  $\text{R}_2$  est alkylène en  $\text{C}_2\text{-C}_6$  et  $n$  est un nombre de 2 à 20 ; et





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dans laquelle  $R_1$  est alkyle en  $C_1-C_8$ , cyclohexyle, benzyle ou alkyle en  $C_2-C_4$  substitué par alcoxy en  $C_1-C_4$  ou diméthylamino ou diéthylamino,  $R_2$  est l'hydrogène ou méthyle, X est morpholino ou un groupe

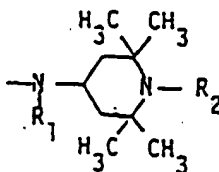
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$-OR_5$  ou un groupe

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dans laquelle  $R_3$  et  $R_4$  qui peuvent être identiques ou différents sont alkyle en  $C_1-C_8$ , cyclohexyle, benzyle ou alkyle en  $C_2-C_4$  substitués par OH, alcoxy en  $C_1-C_4$ , diméthylamino ou diéthylamino,  $R_4$  peut être aussi l'hydrogène et  $R_5$  est alkyle en  $C_1-C_8$ , allyle, cyclohexyle ou benzyle.

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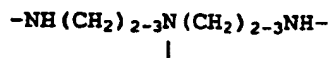
4. Composition de photostabilisants selon la revendication 1 où le composé (A) est pris dans le groupe comprenant des composés de formule (II) dans laquelle  $R_1$  est alkyle en  $C_2-C_8$  ou cyclohexyle,  $R_2$  est l'hydrogène ou alkyle en  $C_2-C_8$ ,  $R_3$  est l'hydrogène ou méthyle,  $R_4$  est  $-(CH_2)_{2-6}-$  et n est un nombre de 2 à 10.

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5. Composition de photostabilisants selon la revendication 1 dans laquelle le composé (A) est pris dans le groupe comprenant les composés de formule (III) dans lesquels  $R_1$  est l'hydrogène ou méthyle,  $R_2$  est  $-(CH_2)_6-$ ,  $R_3$  est  $-(CH_2)_{2-6}-$  et n est un nombre de 2 à 10.

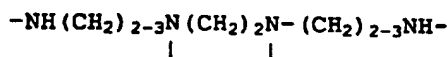
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6. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) est pris dans le groupe comprenant les composés de formule (IV) dans lesquels  $R_1$  est l'hydrogène ou méthyle,  $R_2$  est alkyle en  $C_1-C_4$ , n vaut 2, 3 ou 4, et  $R_3$  est un groupe de formule  $-NH(CH_2)_{2-6}NH-$  pour n = 2,



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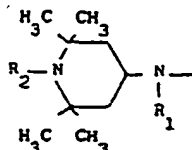
pour n = 3 et



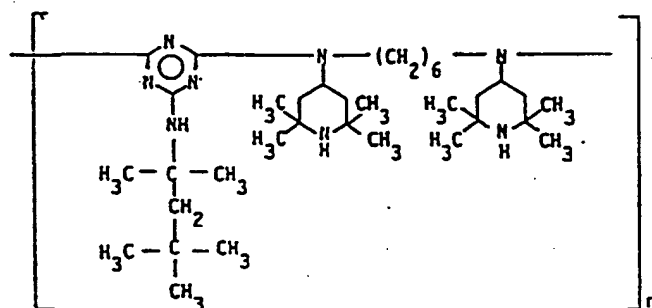
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pour n = 4.

7. Composition de photostabilisants selon la revendication 1 dans laquelle le composé (A) est pris dans le groupe comprenant les composés de formule (V) dans lesquels R est  $-(CH_2)_{2-6}-$  et n est un nombre de 2 à 20.
8. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) est pris dans le groupe comprenant les composés de formule (X) dans lesquels  $R_1$  est l'hydrogène ou méthyle,  $R_2$  est  $-(CH_2)_{2-6}-$  et n est un nombre de 2 à 10.
9. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) est pris dans le groupe comprenant les composés de formule (XXI) dans lesquels  $R_1$  est alkyle en  $C_1-C_8$ ,  $R_2$  est l'hydrogène ou méthyle et X est un groupe

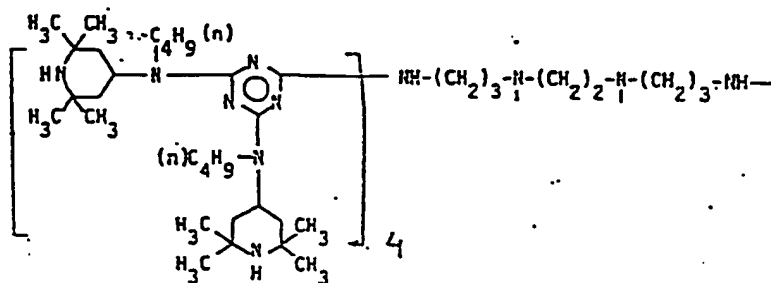


10. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) répond à la formule



ayant une masse moléculaire comprise entre 2000 et 4000.

11. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) répond à la formule



12. Composition de photostabilisants selon la revendication 1, dans laquelle le composé (A) répond à la formule



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de 0,005 à 1 %, de préférence de 0,025 à 0,5 % pour le composé (B) .

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21. Polyéthylène stabilisé selon la revendication 19, dans lequel le pourcentage en poids du composé (C), par rapport au polyéthylène, est de 0,005 à 1 %, de préférence de 0,025 à 0,5 %.
22. Polyéthylène stabilisé selon la revendication 19 lequel est le polyéthylène basse densité (LDPE), le polyéthylène basse densité linéaire (LLDPE) ou un mélange de ces deux composés.
- 10 23. Film préparé à partir du polyéthylène basse densité (LDPE), du polyéthylène basse densité linéaire (LLDPE) ou de mélanges des deux, stabilisé par une composition de photostabilisants de la revendication 1 ou 2.
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